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(54) Title: NITRILE COMPOSITIONS

(57) Abrégé/Abstract:

The present invention relates to a polymer composite comprising at least one carboxylated nitrile rubber polymer, that is optionally hydrogenated, at least one basic compound, at least one polyhalogenated hydrocarbon, optionally at least one filler and optionally at least one cross-linking agent, a process for preparing said polymer composite wherein at least one carboxylated nitrile rubber polymer, that is optionally hydrogenated, at least one basic compound, at least one polyhalogenated hydrocarbon, optionally at least one filler and optionally at least one cross-linking agent are mixed and a shaped article comprising diester bridges formed by reaction of at least one carboxylated nitrile rubber polymer, that is optionally hydrogenated, at least one basic compound and at least one polyhalogenated hydrocarbon.



Abstract

The present invention relates to a polymer composite comprising at
5 least one carboxylated nitrile rubber polymer, that is optionally hydrogenated,
at least one basic compound, at least one polyhalogenated hydrocarbon,
optionally at least one filler and optionally at least one cross-linking agent, a
process for preparing said polymer composite wherein at least one
10 carboxylated nitrile rubber polymer, that is optionally hydrogenated, at least
one basic compound, at least one polyhalogenated hydrocarbon, optionally at
least one filler and optionally at least one cross-linking agent are mixed and a
shaped article comprising diester bridges formed by reaction of at least one
carboxylated nitrile rubber polymer, that is optionally hydrogenated, at least
one basic compound and at least one polyhalogenated hydrocarbon.

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Nitrile Compositions

Field of the Invention.

The present invention relates to a polymer composite comprising at least one carboxylated nitrile rubber polymer, that is optionally hydrogenated, at least one basic compound, at least one polyhalogenated hydrocarbon, optionally at least one filler and optionally at least one cross-linking agent, a process for preparing said polymer composite wherein at least one carboxylated nitrile rubber polymer, that is optionally hydrogenated, at least one basic compound, at least one polyhalogenated hydrocarbon, optionally at least one filler and optionally at least one cross-linking agent are mixed and a shaped article comprising diester bridges formed by reaction of at least one carboxylated nitrile rubber polymer, that is optionally hydrogenated, at least one basic compound and at least one polyhalogenated hydrocarbon.

Background of the Invention

Hydrogenated nitrile rubber (HNBR), prepared by the selective hydrogenation of acrylonitrile-butadiene rubber (nitrile rubber; NBR, a copolymer comprising at least one conjugated diene, at least one unsaturated nitrile and optionally further comonomers), is a specialty rubber which has very good heat resistance, excellent ozone and chemical resistance, and excellent oil resistance. Coupled with the high level of mechanical properties of the rubber (in particular the high resistance to abrasion) it is not surprising that NBR and HNBR have found widespread use in the automotive (seals, hoses, bearing pads) oil (stators, well head seals, valve plates), electrical (cable sheathing), mechanical engineering (wheels, rollers) and shipbuilding (pipe seals, couplings) industries, amongst others.

Summary of the Invention

In one of its aspects, the present invention relates to polymer composites comprising at least one carboxylated nitrile rubber polymer, that is optionally hydrogenated, at least one basic compound, at least one

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polyhalogenated hydrocarbon, optionally at least one filler and optionally at least one cross-linking agent. It is preferred that the NBR is fully or partially hydrogenated ("HNBR"). In particular, the invention relates to polymer composites comprising at least one hydrogenated carboxylated nitrile rubber
 5 polymer, at least one basic compound, at least one polyhalogenated hydrocarbon, optionally at least one filler and optionally at least one cross-linking agent.

In another one of it's aspects, the present invention relates to a process for preparing said polymer composite wherein at least one hydrogenated
 10 carboxylated nitrile rubber polymer, at least one basic compound, at least one polyhalogenated hydrocarbon, optionally at least one filler and optionally at least one cross-linking agent are mixed.

In still another one of it's aspects, the present invention relates to a shaped article comprising diester bridges formed by reaction of at least one
 15 carboxylated nitrile rubber polymer, that is optionally hydrogenated, at least one basic compound and at least one polyhalogenated hydrocarbon.

Brief Description of the Drawings

Fig 1. shows for the compounds of examples 1-4 the torque (S') in dN.m
 20 for the first hour of curing at 1° arc and 160°C.

Description of the Invention

As used throughout this specification, the term "nitrile polymer" or NBR is intended to have a broad meaning and is meant to encompass a copolymer
 25 having repeating units derived from at least one conjugated diene, at least one alpha-beta-unsaturated nitrile, at least one monomer having a carboxylic group and optionally further one or more copolymerizable monomers.

The conjugated diene may be any known conjugated diene, in particular a C₄-C₈ conjugated diene. Preferred conjugated dienes are butadiene, isoprene, piperylene, 2,3-dimethyl butadiene and mixtures thereof. Even more
 30 preferred C₄-C₆ conjugated dienes are butadiene, isoprene and mixtures thereof. The most preferred C₄-C₆ conjugated diene is butadiene.

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The alpha-beta-unsaturated nitrile may be any known alpha-beta-unsaturated nitrile, in particular a C₃-C₅ alpha-beta-unsaturated nitrile. Preferred C₃-C₅ alpha-beta-unsaturated nitriles are acrylonitrile, methacrylonitrile, ethacrylonitrile and mixtures thereof. The most preferred C₃-C₅ alpha-beta-unsaturated nitrile is acrylonitrile.

The monomer having at least one carboxylic group may be any known monomer having at least one carboxylic group being copolymerizable with the nitrile and the diene.

Preferred monomers having at least one carboxylic group are unsaturated carboxylic acids. Non-limiting examples of suitable unsaturated carboxylic acids are fumaric acid, maleic acid, acrylic acid, methacrylic acid and mixtures thereof.

Preferably, the copolymer comprises in the range of from 40 to 85 weight percent of repeating units derived from one or more conjugated dienes, in the range of from 15 to 60 weight percent of repeating units derived from one or more unsaturated nitriles and in the range of from 0.1 to 15 weight percent of repeating units derived from one or more monomers having at least one carboxylic group. More preferably, the copolymer comprises in the range of from 55 to 75 weight percent of repeating units derived from one or more conjugated dienes, in the range of from 25 to 40 weight percent of repeating units derived from one or more unsaturated nitriles and in the range of from 1 to 7 weight percent of repeating units derived from one or more monomers having at least one carboxylic group.

Optionally, the copolymer may further comprise repeating units derived from one or more copolymerizable monomers, such as alkylacrylate, styrene. Repeating units derived from one or more copolymerizable monomers will replace either the nitrile or the diene portion of the nitrile rubber and it will be apparent to the skilled in the art that the above mentioned figures will have to be adjusted to result in 100 weight percent.

Hydrogenated in this invention is preferably understood by more than 50 % of the residual double bonds (RDB) present in the starting nitrile polymer/NBR being hydrogenated, preferably more than 90 % of the RDB are

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hydrogenated, more preferably more than 95 % of the RDB are hydrogenated and most preferably more than 99 % of the RDB are hydrogenated.

The present invention is not restricted to a special process for preparing the hydrogenated carboxylated NBR. However, the HXNBR preferred in this
5 the invention is readily available as disclosed in WO-01/77185-A1. For jurisdictions allowing for this procedure, WO-01/77185-A1 is incorporated herein by reference.

The XNBR as well as the HXNBR which forms a preferred component of the polymer composite of the invention can be characterized by standard
10 techniques known in the art. For example, the molecular weight distribution of the polymer was determined by gel permeation chromatography (GPC) using a Waters 2690 Separation Module and a Waters 410 Differential Refractometer running Waters Millennium software version 3.05.01. Samples were dissolved in tetrahydrofuran (THF) stabilized with 0.025% BHT. The columns used for
15 the determination were three sequential mixed-B gel columns from Polymer Labs. Reference Standards used were polystyrene standards from American Polymer Standards Corp.

The inventive polymer composite further comprises at least one basic compound. The basic compound is not restricted and any known basic
20 compound that under the conditions typically used for rubber mixing is capable of abstracting the proton from the carboxylic group(s) of the monomer having at least one carboxylic group is suitable. Non-limiting examples are alkali metal hydroxides (e.g. LiOH, NaOH, KOH) and alkaline earth metal hydroxides (e.g. Ca(OH)₂, Mg(OH)₂), alkaline earth metal oxides (e.g. MgO, ZnO, CaO), alkali
25 metal carbonates and bicarbonates (e.g. Na₂CO₃, K₂CO₃, NaHCO₃). Usually, part of the basic compound will form a salt with the polymer (e.g. a Na-salt) under the conditions typically used for rubber mixing.

In a typical rubber mixing procedure, the ingredients of the final polymer composite are mixed together, suitably at an elevated temperature that may
30 range from 25 °C to 150 °C. Normally the mixing time does not exceed one hour and a time in the range from 2 to 30 minutes is usually adequate. The mixing is suitably carried out in an internal mixer such as a Banbury mixer, or a Haake or Brabender miniature internal mixer. A two roll mill mixer also

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provides a good dispersion of the additives within the elastomer. An extruder also provides good mixing, and permits shorter mixing times.

The inventive polymer composite further comprises at least one polyhalogenated hydrocarbon. The polyhalogenated hydrocarbon is not
 5 restricted and any known polyhalogenated hydrocarbon is capable of reacting with the polymer salt formed by part of the basic compound and the polymer and thus creating a diester bridge between two polymer chains. Non-limiting examples are dihaloalkanes, dihaloalkenes, dihaloaryls.

Preferred polyhalogenated hydrocarbons are 1,10-dibromodecane, 1,6-
 10 dibromohexane and 1,3-dibromopropane.

It may be advantageous to use polyhalogenated hydrocarbons with one or more additional reactive groups including but not limited to halogens (e.g. trihalohydrocarbons) to increase the formation of ester bridges and thus increase the crosslinking density.

15 The inventive polymer composite further optionally comprises at least one filler. The filler may be an active or an inactive filler or a mixture thereof. The filler may be in particular:

- highly dispersed silicas, prepared e.g. by the precipitation of silicate solutions or the flame hydrolysis of silicon halides, with specific
 20 surface areas of in the range of from 5 to 1000 m²/g, and with primary particle sizes of in the range of from 10 to 400 nm; the silicas can optionally also be present as mixed oxides with other metal oxides such as those of Al, Mg, Ca, Ba, Zn, Zr and Ti;
- synthetic silicates, such as aluminum silicate and alkaline earth
 25 metal silicate like magnesium silicate or calcium silicate, with BET specific surface areas in the range of from 20 to 400 m²/g and primary particle diameters in the range of from 10 to 400 nm;
- natural silicates, such as kaolin and other naturally occurring silica;
- glass fibers and glass fiber products (matting, extrudates) or glass
 30 microspheres;
- carbon blacks; the carbon blacks to be used here are prepared by the lamp black, furnace black or gas black process and have preferably BET (DIN 66 131) specific surface areas in the range of

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from 20 to 200 m²/g, e.g. SAF, ISAF, HAF, FEF or GPF carbon blacks;

- rubber gels, especially those based on polybutadiene, butadiene/styrene copolymers, butadiene/acrylonitrile copolymers and polychloroprene;

or mixtures thereof.

Examples of preferred mineral fillers include silica, silicates, clay such as bentonite, gypsum, alumina, titanium dioxide, talc, mixtures of these, and the like. These mineral particles have hydroxyl groups on their surface, rendering them hydrophilic and oleophobic. This exacerbates the difficulty of achieving good interaction between the filler particles and the rubber. For many purposes, the preferred mineral is silica, especially silica made by carbon dioxide precipitation of sodium silicate. Dried amorphous silica particles suitable for use in accordance with the invention may have a mean agglomerate particle size in the range of from 1 to 100 microns, preferably between 10 and 50 microns and most preferably between 10 and 25 microns. It is preferred that less than 10 percent by volume of the agglomerate particles are below 5 microns or over 50 microns in size. A suitable amorphous dried silica moreover usually has a BET surface area, measured in accordance with DIN (Deutsche Industrie Norm) 66131, of in the range of from 50 and 450 square meters per gram and a DBP absorption, as measured in accordance with DIN 53601, of in the range of from 150 and 400 grams per 100 grams of silica, and a drying loss, as measured according to DIN ISO 787/11, of in the range of from 0 to 10 percent by weight. Suitable silica fillers are available under the trademarks HiSil® 210, HiSil® 233 and HiSil® 243 from PPG Industries Inc. Also suitable are Vulkasil® S and Vulkasil® N, from Bayer AG.

Often, use of carbon black as a filler is advantageous. Usually, carbon black is present in the polymer composite in an amount of in the range of from 20 to 200 parts by weight, preferably 30 to 150 parts by weight, more preferably 40 to 100 parts by weight. Further, it might be advantageous to use a combination of carbon black and mineral filler in the inventive polymer composite. In this combination the ratio of mineral fillers to carbon black is usually in the range of from 0.05 to 20, preferably 0.1 to 10.

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The polymer composite may advantageously further comprise other natural or synthetic rubbers such as BR (polybutadiene), ABR (butadiene/acrylic acid-C₁-C₄-alkylester-copolymers), CR (polychloroprene), IR (polyisoprene), SBR (styrene/butadiene-copolymers) with styrene contents in the range of 1 to 60 wt%, NBR (butadiene/acrylonitrile-copolymers with acrylonitrile contents of 5 to 60 wt%, HNBR with a Mooney viscosity (ML 1+4 @ 100°C according to ASTM test D1646) of at least 30 (partially or totally hydrogenated NBR-rubber), EPDM (ethylene/propylene/diene-copolymers), FKM (fluoropolymers or fluororubbers), olefin-vinylacetate-copolymers (e.g. LEVAPREN™), olefin-vinylacrylate-copolymers (e.g. VAMAC®) and mixtures of the given polymers. Careful blending with conventional HNBR often reduces cost of the polymer composite without sacrificing the processability. The amount of conventional HNBR and/or other natural or synthetic rubbers will depend on the process condition to be applied during manufacture of shaped articles and is readily available by few preliminary experiments.

The polymer composite furthermore optionally comprises one or more cross-linking agents or curing systems. The invention is not limited to a special curing system, however, peroxide curing system are preferred. Furthermore, the invention is not limited to a special peroxide curing system. For example, inorganic or organic peroxides are suitable. Preferred are organic peroxides such as dialkylperoxides, ketalperoxides, aralkylperoxides, peroxide ethers, peroxide esters, such as di-tert.-butylperoxide, bis-(tert.-butylperoxyisopropyl)-benzene, dicumylperoxide, 2,5-dimethyl-2,5-di(tert.-butylperoxy)-hexane, 2,5-dimethyl-2,5-di(tert.-butylperoxy)-hexene-(3), 1,1-bis-(tert.-butylperoxy)-3,3,5-trimethyl-cyclohexane, benzoylperoxide, tert.-butylcumylperoxide and tert.-butylperbenzoate. Usually the amount of peroxide in the polymer composite is in the range of from 1 to 10 phr (= per hundred rubber), preferably from 4 to 8 phr. Subsequent curing is usually performed at a temperature in the range of from 100 to 200 °C, preferably 130 to 180 °C. Peroxides might be applied advantageously in a polymer-bound form. Suitable systems are commercially available, such as Polydispersion T(VC) D-40 P from Rhein Chemie Rheinau GmbH, D (= polymerbound di-tert.-butylperoxy-isopropylbenzene).

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The rubber composition according to the invention can contain further auxiliary products for rubbers, such as reaction accelerators, vulcanizing accelerators, vulcanizing acceleration auxiliaries, antioxidants, foaming agents, anti-aging agents, heat stabilizers, light stabilizers, ozone stabilizers, processing aids, plasticizers, tackifiers, blowing agents, dyestuffs, pigments, waxes, extenders, organic acids, inhibitors, metal oxides, and activators such as triethanolamine, polyethylene glycol, hexanetriol, etc., which are known to the rubber industry. The rubber aids are used in conventional amounts, which depend inter alia on the intended use. Conventional amounts are e.g. from 0.1 to 50 wt.%, based on rubber. Preferably the composition comprises in the range of 0.1 to 20 phr of an organic fatty acid as an auxiliary product, preferably a unsaturated fatty acid having one, two or more carbon double bonds in the molecule which more preferably includes 10% by weight or more of a conjugated diene acid having at least one conjugated carbon-carbon double bond in its molecule. Preferably those fatty acids have in the range of from 8-22 carbon atoms, more preferably 12-18. Examples include stearic acid, palmitic acid and oleic acid and their calcium-, zinc-, magnesium-, potassium- and ammonium salts. Preferably the composition comprises in the range of 5 to 50 phr of an acrylate as an auxiliary product. Suitable acrylates are known from EP-A1-0 319 320, in particular p. 3, l. 16 to 35, from US-5 208 294, in particular Col. 2, l. 25 to 40, and from US-4 983 678, in particular Col. 2, l. 45 to 62. Particular reference is made to zinc acrylate, zinc diacrylate or zinc dimethacrylate or a liquid acrylate, such as trimethylolpropanetrimethacrylate (TRIM), butanedioldimethacrylate (BDMA) and ethylenglycoldimethacrylate (EDMA). It might be advantageous to use a combination of different acrylates and/or metal salts thereof. Of particular advantage is often to use metal acrylates in combination with a Scorch-retarder such as sterically hindered phenols (e.g. methyl-substituted aminoalkylphenols, in particular 2,6-di-tert.-butyl-4-dimethylaminomethylphenol).

The ingredients of the final polymer composite are mixed together, suitably at an elevated temperature that may range from 25 °C to 200 °C. Normally the mixing time does not exceed one hour and a time in the range from 2 to 30 minutes is usually adequate. The mixing is suitably carried out in

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an internal mixer such as a Banbury mixer, or a Haake or Brabender miniature internal mixer. A two roll mill mixer also provides a good dispersion of the additives within the elastomer. An extruder also provides good mixing, and permits shorter mixing times. It is possible to carry out the mixing in two or
5 more stages, and the mixing can be done in different apparatus, for example one stage in an internal mixer and one stage in an extruder. However, it should be taken care that no unwanted pre-crosslinking (= scorch) occurs during the mixing stage, but that the conditions are suitable for the desired esterification process involving polymer, basic compound and polyhalogenated
10 hydrocarbon. For compounding and vulcanization see also: Encyclopedia of Polymer Science and Engineering, Vol. 4, p. 66 et seq. (Compounding) and Vol. 17, p. 666 et seq. (Vulcanization).

This process provides thermally resistant flexible cross-linking between the polymer chains. This new cross-linking system may be used in
15 applications where a carboxylated polymer is used such as rolls, seals, belts or rings.

Furthermore, the invention provides a shaped article comprising said inventive polymer composite comprising diester bridges. Preferred shaped articles are a seal, hose, belt, roller, bearing pad, stator, well head seal, valve
20 plate, cable sheathing or pipe seal.

Furthermore, the inventive polymer composite is very well suited for wire and cable production.

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EXAMPLES**Example 1 - 4**

Polymer composites were mixed in a brabender miniature internal mixer in a single mixing step (all ingredients included at the start of the procedure, 6 minutes mix cycle, 55 rpm, start temperature 30°C, max temperature 125°C). The formulations used in this assessment are based on a simplified recipe according to Table 1.

Armeen™ 18d is octadecylamine available from AkzoNobel and is used to reduce compound stickiness to metal.

10 **Table 1 Compounding Recipe**

Example	1 (Comp.)	2 (Comp.)	3	4
Therban XT 8889	100	100	100	100
Armeen 18d	0.5	0.5	0.5	0.5
1,10-dibromodecane (Aldrich)	5		5	2.5
NaOH (Aldrich)		2.5	2.5	2.5

Polymer Composites Properties

Table 2 shows a summary of the properties of polymer composites of Exp. 1-4. Examples 1-2 are for comparison. MDR Cure Properties (160°C, 1° arc, 1.7 Hz, 60 minutes). The complete graphs for the torque are shown in Fig. 1.

15 **Table 2 MDR Cure Properties**

Example	1	2	3	4
Maximum Torque (MH, dN.m)	2.57	7.88	28.75	20.7
Minimum Torque (ML, dN.m)	1.27	5.26	6.2	6.01
Delta MH-ML (dN.m)	1.3	2.62	22.55	14.6

20 The Delta MH-ML gives an indication of the crosslinking density. It is clear from examples 3-4 that the presence of both a base (e.g. NaOH) and a polyhalogenated hydrocarbon (e.g. 1,10-dibromodecane) is required. The presence of both components results in a significant increased in cure density.

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Claims

1. A polymer composite comprising at least one, optionally hydrogenated, carboxylated nitrile rubber polymer, at least one basic compound, at least one polyhalogenated hydrocarbon, optionally at least one filler and optionally at least one cross-linking agent.
2. A composite according to claim 1 wherein the carboxylated nitrile rubber polymer is a hydrogenated carboxylated nitrile rubber.
3. A composite according to claim 1 or 2 wherein the basic compound is an alkali metal hydroxide, oxide, carbonate or bicarbonate or an alkaline earth metal hydroxide, oxide or carbonate.
4. A composite according to any of claims 1-3 wherein the polyhalogenated hydrocarbon is a polyhalogenated alkane, polyhalogenated alkene, or polyhalogenated aryl.
5. A composite according to any of claims 1-4 wherein the polyhalogenated hydrocarbon is a dibromoalkane.
6. A composite according to any of claims 1-5 wherein the polymer composite comprises a peroxide, resin or sulfur curing system.
7. A composite according to any of claims 1-5 wherein the polymer composite further comprises at least one polymer selected from the group consisting of NBR, HNBR, olefin-vinylacrylate-copolymers and olefin-vinylacetate-copolymers.
8. A process for preparing a polymer composite according to any of claims 1-6 wherein at least one, optionally hydrogenated, carboxylated nitrile rubber polymer, at least one basic compound, at least one

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polyhalogenated hydrocarbon, optionally at least one filler and optionally at least one cross-linking agent are mixed.

5 9. A shaped article comprising at least one, optionally hydrogenated, carboxylated nitrile rubber polymer crosslinked by diester bridges.

10. A shaped article according to claim 9, wherein the article is a seal, hose, belt, roller, bearing pad, stator, well head seal, valve plate, cable sheating or pipe seal.

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Fig. 1

